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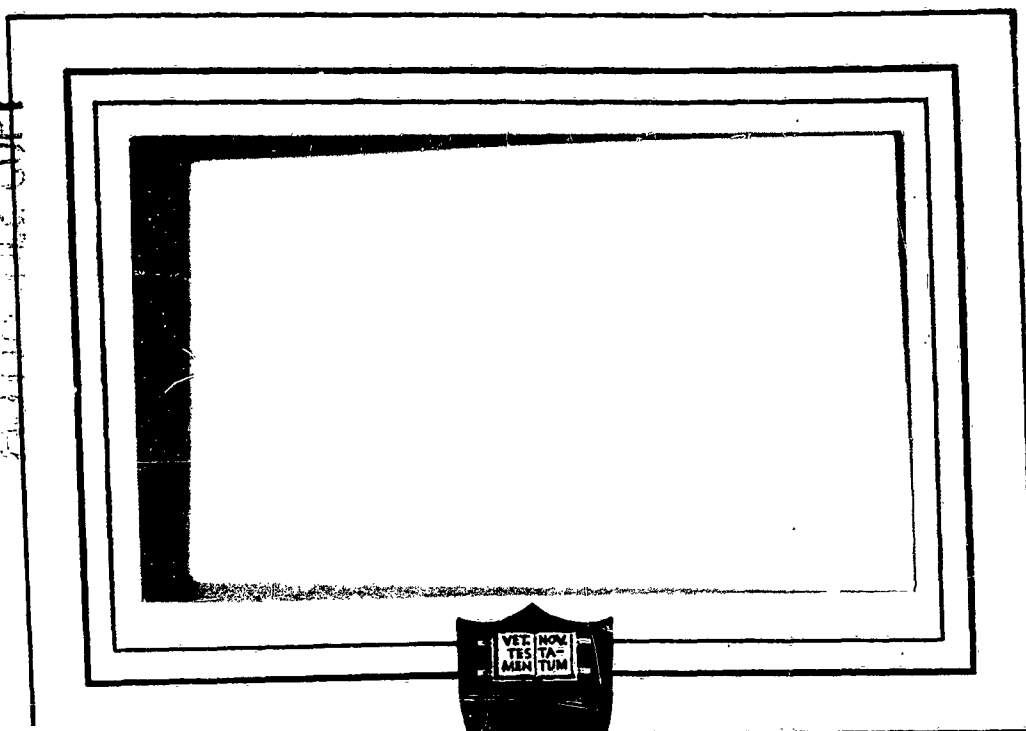
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Contract AF 49(638)-411

A TECHNICAL REPORT ON
THE MECHANISM OF IGNITION OF COMPOSITE SOLID
PROPELLANTS BY HOT GASES

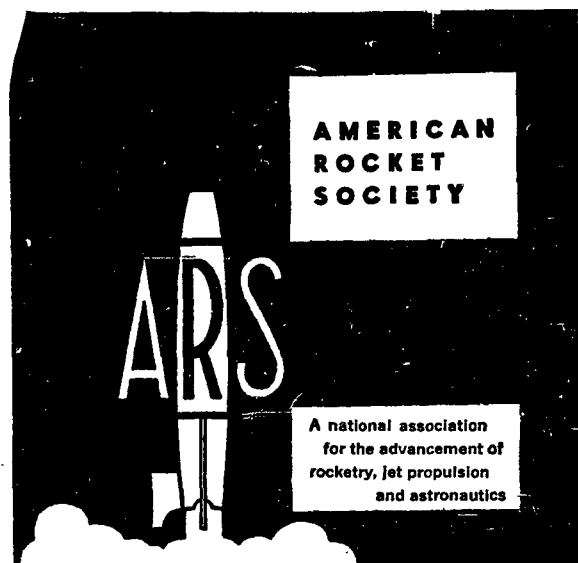
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4 April 1960

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THE MECHANISM OF IGNITION OF COMPOSITE SOLID PROPELLANTS
BY HOT GASES

by

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BY HOT GASES

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ABSTRACT

Ignition of composite solid propellants of the ammonium perchlorate type has been accomplished in a shock tube filled with a mixture of oxygen and nitrogen. The time to ignition, that is, the time interval between the instant of contact of the propellant sample by hot gas and the subsequent emission of light as detected by a photocell, has been measured as a function of oxygen concentration for several different propellants. It was found that the ignition times varied inversely with the oxygen concentration. A new theoretical approach has been developed for the ignition of a composite propellant by a hot gas, the essential element of which is that the flame first starts in the gaseous layer adjacent to the propellant. The observed ignition delay is simply the time required for enough fuel to vaporize to create a combustible gaseous mixture. The theory explains the trend of the experimental data quite well. The theory suggests certain directions for improving the ignition capability of practical igniters and for enhancing the ignitability of solid propellants.

A. Introduction

A solid rocket is usually ignited by suddenly bringing an intense source of heat in contact with the exposed surface of the propellant grain. Practical igniters of many forms and sizes have been developed in the past and are in use today. In general, an igniter is a single assembly installed in the loaded rocket chamber that is capable of producing a flame after receiving an electrical impulse. This flame, directed at the grain surface, is designed to ignite the grain in a small fraction of a second. The objectives of igniter design are to minimize the

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weight and size of the igniter for a given rocket engine, to minimize the ignition delay, to avoid initial over-pressures, and to ensure effective ignition of upper rocket stages in empty space environment. To achieve these objectives most completely, the basic process of ignition must be understood.

Other than the general principle that sustained heat causes ignition, nothing substantial has been known in the recent past about the physics of ignition of solid propellants. Lately, however, some elementary experiments have been carried out, in which test samples have been exposed to various forms of heat input of measured amount, with the object of measuring ignition delay as a function of heat input conditions (Ref. 1, 2, 3, 4). Correlations have been made with limited success on the hypothesis that ignition takes place when the surface temperature reaches a level high enough to stimulate a critical rate of heat generation in the solid phase. This theory was developed in its most complete form by Hicks (Ref. 5).

This hypothetical mechanism, a run-away reaction in the solid phase, has never been actually verified. On the contrary, experimental evidence began to build up, pointing to the importance of gas phase reactions (Ref. 2, 6). In particular, the previously observed effect of oxygen in the surrounding gas in speeding up the ignition process cannot be incorporated in a theory that depends on solid phase reactions alone. Furthermore, there is the theoretical and experimental evidence that the steady-state flame is one in which the bulk of the heat release occurs in a gaseous reaction zone adjacent to the solid surface (Ref. 7, 8, 9). It would seem that, for a theory of ignition to be acceptable, it should explain the transition from the initial development of the flame to its ultimate steady-state structure. The solid phase ignition theory is obscure on this point.

This paper describes a research program in two parts: an experimental project designed to measure ignition delays of test propellants under precisely controlled heating conditions, and a theoretical study aimed at calculating the ignition delay on the basis of a gas phase ignition mechanism. The discussion of the theory is taken up in Section C. Some general remarks about the nature of the experiments are presented here.

In practice, an ignition imparts energy to the exposed propellant surface in several ways simultaneously: (1) heat transfer by forced convection or simple conduction; (2) diffusion of condensible metallic vapors or of energetic radicals from the igniter flame to the cool propellant surface, a process actually joined to (1); (3) transport of heat by hot refractory particles that impinge on the propellant surface and create local centers of ignition; (4) thermal radiation absorption; (5) photochemical absorption. In designing a controlled ignition experiment, any one of these energy transfer processes can be singled out. The most convenient for this purpose are conduction from hot wires (Ref. 1), conduction from hot gases, convective heating by hot gas (Ref. 2, 3, 4), and thermal radiation (Ref. 10).

In the present experiments, a shock tube is used to generate a hot gas in contact with the propellant. Several configurations are possible. One is to mount the propellant sample in the form of a sharp or blunt nose streamline model on a sting in the center of the tube and allow the hot gas following the shock to first sweep past the model and then envelop it after the return of the reflected shock. This was tried in the early phase of this program (Ref. 11). Although ignition could be accomplished repeatedly in the manner in times of the order of 1 millisecond, it was found that the precise instant of ignition could not be determined reliably even with a photocell detector. A plausible explanation of the difficulty

is that the initial flame in the gaseous boundary layer is swept downstream and quenched before appreciable light emission takes place. This method of testing has therefore been set aside. A second arrangement is to place the propellant sample flush with the wall in an outflow duct leading from the end of the shock tube. This is the method employed by Ryan et al (Ref. 3). The boundary layer is thicker in this set up and eventually permits the establishment of a flame. The most rapid ignition is obtainable with a flat sample mounted flush in the end wall of the tube, the arrangement used in the present experiments. Ignition times of the order of 1 millisecond and less are measured. This is attributable to the stagnant state of the gaseous reaction zone. An attractive feature of the end-wall arrangement is that it can be analyzed theoretically quite simply because of its one dimensionality.

It should be noted, in passing, that ignition in a shock tube on a go or no-go basis can be readily developed into a control test for ignitability of an experimental propellant.

B. Experimental Method

A shock tube technique was employed to produce an environment suitable to cause ignition of the various solid propellant specimens subject to test. The specific heating condition depends on the location and configuration of the solid propellant model as well as the operating condition of the shock tube, i.e., shock wave Mach number M_s , and initial pressure of the test gas, P_0 . The test gas reactivity was varied by changing the weight fraction of oxygen in a test gas mixture of O_2 and N_2 .

The 1.6 in. I.D. stainless steel shock tube is comprised of a pressure section (10') and a test section (8'). To set the tube into operation an aluminum burst diaphragm, initially separating the two sections, is ruptured by slowly increasing the helium pressure until the diaphragm fails, allowing the helium to rush into the test section and compress the test gas before it. The compression wave rapidly (within a few tube diameters) builds into a shock wave which propagates down the test section setting into motion the hot overtaken test gas. The velocity of shock wave propagation divided by the speed of sound of the uncompressed test gas is defined as the Mach number of the shock wave (M_s).

The ratio of shock gas to unshocked gas temperature, density, and pressure as well as imparted velocity all increase with M_s . This important experimental parameter depends only on the ratio of helium pressure to test gas pressure at the instant of diaphragm rupture. Increasing this ratio increases the M_s .

The nature of the heating exposure received by a test sample depends on its location in the tube. Only conductive heating is experienced by flat surface propellant models mounted flush with the end wall of the shock tube while convective heating is experienced by pointed models positioned along the axis of the tube (Fig. 1). If the end of the tube is open the sting mounted model is exposed to convective heating as the hot shocked gas streams over its surface followed by convective cooling when the cold helium front arrives. Although there is evidence that this heating followed by cooling situation does produce ignition, it was difficult to detect ignition times by means of high speed photographic techniques. Positive ignition was achieved by closing the tube with an end wall causing the incident shock wave to reflect, return to the model position, and stagnate the following test gas before the cold front arrives (Ref. 11).

The period of convective heating represents less than 5% of the 5 milli-seconds useful testing period--that is, the interval between arrival of the incident shock wave and the arrival of the expansion wave (which is generated by the diaphragm rupture, propagates through the pressure section, reflects, and arrives at the end of test section to produce an unsteady, uncontrolled environment). End wall mounted samples are exposed only to conductive heating from the stagnant, twice-shocked gas behind the reflected shock wave during the testing period.

The end wall heating produces a step increase of end wall temperature, the level of which depends on both the M_s and P_o . For a constant P_4 the end wall temperature at first increases as the $T_g(M_s)$ increases, but eventually any incremental decrease in pressure required to produce a greater M_s results in a decrease of density sufficient to reduce the product $(\rho_g)^{1/2} T_g$ to which the end wall temperature jump responds. Since the ignition lags of solid propellants are sensitive to pressure as well as temperature, the useful range of exposure conditions was found to lie between $M_s = 2.5$, $T_s = 380^\circ\text{K}$, $T_g = 1000^\circ\text{K}$, $P_g = 1100$ psi and $M_s = 4.5$, $T_s = 520^\circ\text{K}$, $T_g = 2500^\circ\text{K}$, $P_g = 400$ psi for the small shock tube. The measured end wall temperature was found to be about twice the experimentally predicted value in this range.

Luminosity is used as an indication of ignition. The instant of ignition is taken as the time at which the incipient flame produces a detectable quantity of light. A special high-framing-rate camera was found useful to reveal the details of the ignition process such as site of ignition, flame spreading, etc. (Fig. 3, 4), but in order to make quantitative measurements of ignition times the first response of a scanning vacuum phototube was arbitrarily selected (Fig. 5). Test gas mixtures containing a high percentage of O_2 (i.e., greater than 65%) produced a great deal of radiation upon passage of the reflected shock wave. There is some evidence that this is caused by burning of dust particles or other contaminants which find their way into the tube. A careful cleaning of the tube before each run reduced this to a tolerable level (Fig. 5). Of the various filters and photo sensing devices tested it was found that an RCA 935 type vacuum phototube used in conjunction with a Kodak Wratten 18-A type filter produced the cleanest ignition signal. Further reduction of shock-wave induced luminosity was possible by placing apertures in the optical path between the igniting model and scanning photocell which limits the field of view to the propellant sample, thereby reducing the stray radiation from the background gas.

Three types of sting mounted samples have been employed. The tip of the model is located $2\frac{5}{4}$ " from the end wall on the end of a slender stainless steel sting. Both sting and model have a $5/32$ " O.D. They were either conically tipped (38° total included angle) or round nose ($5/64$ " radius). Occasionally, an inert aluminum-tipped conical model is used. In the end wall mounted configuration a $1/4$ " diameter cylinder of propellant is recessed into the end wall of the tube to a depth of $1/4$ ", the exposed end of the sample being flush with the wall.

It was found that the juncture between the propellant sample and its mount was an ignition-sensitive region. That is, if the impinging shock wave were allowed to penetrate into an exposed crack between the propellant model and its mount uncontrolled convective heating would lead to a spuriously rapid ignition (Fig. 4). When an inorganic cement of water glass and asbestos covered this region the edge effect disappeared.

The data presented in Fig. 10 represents experimental ignition time lags of two types of ammonium perchlorate propellants. Both the polyester-styrene

(P-13, Rohm and Haas) and the epoxy (Epon #562, Shell Chemical Company) fuels were mixed with four times their weight of perchlorate to formulate these test samples. Initially, the shock tube was operated to produce the same experimental exposure conditions ($M_s = 3.0$, $P_g = 700$ psi, $T_g = 1400^\circ\text{K}$, $T_s = 432^\circ\text{K}$) while the oxygen weight fraction of the test gas composition was varied. This changed the reactivity of the surrounding atmosphere while keeping the thermal exposure constant.

C. Theory of Ignition of Hot Gas

The theory treats the case of a propellant sample mounted in the end wall of the shock tube, with its exposed surface flush with the wall. The normal shock propagates through an igniting gas that fills the downstream part of the shock tube, and is then reflected from the end wall. The ignition delay is recorded as the time from the moment of reflection to the moment of first detection of light from the incipient flame on the propellant surface.

Heat starts flowing into the propellant surface at the moment of reflection. In a time that is very short compared to the ignition delay, a stagnant column of hot gas at temperature T_g is created adjacent to the propellant, and a steady-state interfacial temperature T_s is established (Fig. 2). (Actually, because two different substances, oxidizer and fuel, are exposed at the surface, consideration should be given to two different T_s values. However, there is evidence that below 600°K the usual fuel components vaporize much more rapidly than ammonium perchlorate, so that it is legitimate to simplify the theory by considering only the exposed fuel surfaces as the source of reactable vapor (Fig. 8). The perchlorate is taken into account only as an obstruction, that is, its presence reduces the amount of exposed propellant area that is effective.) Thus, starting immediately after reflection of the shock, the gas adjacent to the solid surface starts cooling off and a "cold wave" propagates upstream at a rate governed by heat conduction laws. At the same time pyrolyzed fuel vapor generated at the heated fuel surface propagates upstream at a rate governed by the laws of mass diffusion (Fig. 6). If oxygen is contained in the igniting gas, the first flame will begin as a result of reaction between the fuel vapor and the gaseous oxygen. (If no free oxygen is contained in the igniting gas, much more intense heating will be required to decompose the oxidizer and thus generate some oxygen, or to bring the oxidizer crystals into the zone of hot fuel vapor.) The first flame will occur only after a certain time delay, that is, the time required for a certain minimum weight fraction of fuel vapor, Z_f , to overtake the receding region of high temperature T^* in the igniting gas (Fig. 7). This will occur at a certain distance X_{ign}^* shown in Fig. 7. In identifying this time interval with the observed ignition delay as described in Section B, the tacit assumption is made that there is very little time between the instant a run-away oxidation rate is attained somewhere on the gas phase and the emission of sufficient light to actuate the photocell detection system.

Some simplifying assumptions enter into the analysis. Heat flow is by pure conduction in a stagnant gas, that is, no convection. The density of the gas does not change during the cooling down process near the propellant. The outward flow of fuel vapor by diffusion does not modify the temperature distribution or oxygen concentration, that is, the actual flow is very small. The pressure remains uniform in the gas zone of interest. The gaseous oxidation reaction is bimolecular, and the incipient reaction does not modify the temperature distribution or concentration distribution in the gas phase. The rate of vaporization of the fuel from the surface is controlled by an Arrhenius type rate law and is not limited by the rate of heat flow from the hot gas to the surface.

The temperature distribution in the hot gas, neglecting chemical reaction, follows this equation (Ref. 17):

$$\frac{T - T_s}{T_g - T_s} = \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_g t}}\right) \quad (1)$$

where x is the distance from the surface, t the time after reflection and α_g , the thermal diffusivity in the gas phase (assumed independent of T).

The temperature at the surface remains constant with time, as is shown by heat conduction theory (Ref. 17):

$$\frac{T_s - T_0}{T_g - T_s} = \left(\frac{\lambda_g \rho_g c_g}{\lambda_f \rho_f c_f} \right)^{1/2} \quad (2)$$

The concentration of fuel vapor C_f (mass/unit volume) in the space near the fuel surface is given by the following solution of the diffusion equation (Ref. 18):

$$C_f = \frac{2\dot{m}_f t^{1/2}}{D_{12}^{1/2}} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{12} t}}\right) \quad (3)$$

where D_{12} is the molecular diffusivity of fuel vapor into the adjacent ignition gas. (To be specific, it is impossible for the gasified fuel to have a molecular weight as large as that of the solid polymer. Instead, it is reasonable to suppose that the vapor consists of pyrolysis products similar in molecular weight to propane. In the numerical computation below, propane diffusivity in air is used, Ref. 13).

The mass flow per unit area from the surface of the fuel can be expressed as an Arrhenius function, according to Ref. 16:

$$\dot{m}_f = v_f \rho A_f \exp\left(\frac{-E_f}{RT_s}\right) \quad (4)$$

where A_f is the pre-exponential factor expressed as a linear velocity, as in the cited reference, and v is the volumetric fraction of fuel in the propellant mixture.

The preceding four equations are sufficient to describe the fuel concentration and temperature distributions in the gas phase at any time after reflection of the shock. Then, on the assumption that the fuel at each point in space is reacting with the oxygen and thereby generating heat, the temperature at each point varies with time as a result of heat conduction and chemical reaction. This is shown in the following differential equation:

$$\rho_g C_g \frac{\partial T}{\partial t} = \lambda_g \left(\frac{\partial^2 T}{\partial x^2} \right) + q_f C_f C_o A_g \exp\left(\frac{-E_g}{RT}\right) \quad (5)$$

where q_f is the heat of combustion of the fuel per unit mass, A_g and E_g are the usual Arrhenius factors, and C_f and C_o are the fuel and oxygen concentrations expressed in units of mass/unit volume. In this equation, the chemical heat generation term is treated as a small perturbation, that is, the temperature distribution given by Equation (1) is assumed to hold in spite of the fact that it is an exact solution of the differential equation without the heat generation term.

Equation (5) is now used to develop a criterion for the instant of ignition, $t = \tau$. By inserting the T function of Equation (1) into the first term on the right, and inserting Equation (3) into the second term for C_f , it can be shown that $(\partial T / \partial t)$ is negative for all x for a short period after shock reflection ($t = 0$). However, after a period of time, the sum of the two terms turns out to be positive in a narrow x interval. Detailed analysis shows that there is a certain minimum time before $(\partial T / \partial t)$ turns positive, and this occurs at a particular stand-off distance x^* . This is the beginning of the runaway reaction that can be called ignition. Of course, at this instant, the perturbation term of Equation (5) is no longer small, and the solution method employed here is not strictly valid, but analysis of a similar question in Ref. 5 showed that the result is quite accurate, nevertheless.

At any time t greater than τ , the x interval within which $(\partial T / \partial t)$ is positive can be expressed as an interval in ϕ , where ϕ is $x / 2\sqrt{\alpha_g t}$, a dimensionless distance. The ϕ interval for each time t is shown in Fig. 9. The minimum time t is shown by example for the case of $L_{12} = 2.65$, the ratio of fuel vapor diffusivity into the igniter gas to the thermal diffusivity of the igniter gas. (The value shown for L_{12} applies to propane diffusing into air.) The calculated formula for τ , on the basis of the above-described analysis, is:

$$\tau = \left[\frac{(T_2 - T_1) C_g \alpha_g^{1/2}}{2 q_f \nu_f \rho_f A_f \exp\left(\frac{-E_f}{RT_1}\right) A_g \exp\left(\frac{-E_g}{RT_1}\right)} \right]^{2/3} \frac{F(\phi^*, L_{12})}{(Z_o)^{2/3}} \quad (6)$$

where $F(\phi^*, L_{12})$ is defined and evaluated in Fig. 9, and the function K is the reciprocal of the quantity in square brackets. The mass concentration C_o has been replaced by the product of Z_o , the mass fraction of oxygen, and ρ_g , the density of the gas mixture. The temperature T in the Arrhenius function for the rate of oxidation has been replaced by the value T_g . The correction factor ϵ to take care of this substitution has been absorbed in the F function, since ϵ depends on ϕ^* .

The stand-off distance X^* where ignition occurs is readily calculated in terms of ϕ^* , which can be read from Fig. 9:

$$X_{ign}^* = \phi^* \cdot 2 \sqrt{\alpha_g \tau} \quad (7)$$

The orders of magnitude of τ and X_{ign}^* can be computed from physical and chemical properties obtainable from the literature. From the rate of combustion of a gasoline-type fuel in a homogeneous reactor, the required values of A_g and E_g can be taken (Ref. 12). (The value of A_g is slightly altered to fit the observed rates to a second-order reaction rate expression and to adapt it to a fuel having the molecular weight of propane.) The values of A_f and E_f are taken from unpublished work (Ref. 15) on the linear pyrolysis rate of P-13 fuel (a copolymer based on polystyrene), similar to the work of Ref. 16. This information is reproduced in Fig. 8. The tests described in Section D were all performed at these conditions: helium pressure in driver section, 980 psi, nitrogen-oxygen pressure in driven section, 14.7 psi, shock Mach number, 3.

The following numerical values were used:

T_g	= 1400K	Z_o	= 1.00 (pure oxygen case)
T_s	= 432K (estimated)	Q_f	= 12 kcal/gm
C_g	= 0.291 cal/gm K	ρ_f	= 1.12 gm/cc
ρ_g	= 1.23×10^{-2} gm/cc	A_f	= 24.0 cm/sec
α_g	= 0.05 cm ² /sec	E_f	= 11.2 kcal/g mole
$L_{1/2}$	= 2.65	A_g	= 1.0×10^{15} (gm/cc) ⁻¹ sec ⁻¹
γ	= 0.30 (80:20 propellant)	E_g	= 40.0 kcal/g mole

From Fig. 9, the value of $F(\phi^*, L_{1/2})$ is found to be 55. The corresponding value of ϕ_{ign}^* is 0.94. With these numbers inserted into Equations (6) and (7), the ignition time τ comes out 2.0 milliseconds. The stand-off distance X^* of the ignition flame is 0.19 millimeters. From Equations (3) and (4) the mass fractions of fuel vapor at this moment is 5×10^{-15} at the ignition zone X^* , and about 2×10^{-4} adjacent to the surface. Small as these concentrations are, the rate of temperature rise at the station X^* is calculated to be about 10^5 degrees/sec, that is, a fast run-away condition.

The experimental program is designed to test the predictions that can be deduced from the above theoretical reasoning:

1. The ignition delay for P-13 perchlorate propellant is expected to be of the order of 2 milliseconds in pure oxygen.
2. A sample of pure P-13 fuel should ignite under these circumstances more rapidly than the propellant, that is, in about half the time. The same obstruction effect would lengthen the ignition delay time of aluminized propellants.
3. The ignition delay should vary inversely as the 2/3 power of the mass fraction of oxygen in the igniter gas.
4. Under the same shock conditions, it should be almost impossible to ignite the propellant in pure nitrogen, notwithstanding the availability of oxygen in the perchlorate.

5. Ignitability should be almost insensitive to perchlorate particle size under these conditions.

6. Ignitability should be greater for a propellant compounded of a more easily pyrolyzed fuel than P-13, other factors held constant.

7. Ignition delay should vary inversely with the pressure becoming very long at low pressures.

8. For a propellant compounded of an easily pyrolyzed fuel plus perchlorate, ignition in a hot inert gas can be achieved but more severe and more prolonged heating conditions will be required than with oxygen in the gas, in order to pyrolyze the perchlorate and thereby supply the needed oxygen in the gas phase. For a propellant with a hard-to-pyrolyze fuel, the effect of oxygen in the igniter gas will be less pronounced.

9. Catalysts for ignition should turn out to be those that are effective for gas phase oxidation.

10. The variation of ignition delay with T_s may yield a value of E_f for comparison with Ref. 16.

D. Experimental Results and Comparison with Theory

Measurements of ignition delay have been made with the shock tube apparatus described in Section B. The ignition delay is recorded as the time interval between the incidence of the shock wave on the propellant sample and the first light emission indicated by the viewing phototube.

Although many tests have already been performed showing that propellants of various types can be ignited in this manner, the reproducibility of the ignition delays has not been good enough to provide critical tests of all the predictions of the theory. The tests that have been made so far give the following results:

1. Ignition delays with oxygen-containing gas ranged from several tenths of a millisecond to a few milliseconds, in agreement with the computation in Section C.
2. No perchlorate propellant was ignitable in the manner in a pure nitrogen atmosphere.
3. Ignition tests with samples of solid fuel in oxygen-containing gas were generally shorter than with the same fuels in a propellant matrix.
4. The ignition delays of typical ammonium perchlorate propellants varied inversely as the weight fraction of oxygen in the gas, although the exact two-thirds power demanded by Equation (6) did not emerge, (Fig. 10). However, in view of the still unresolved difficulties in making exact measurements of the ignition delay, no serious conflict with the theory is seen on this score.

All of these results are consistent with the predictions of the gas-phase ignition theory. Experiments are continuing to improve the measurements of delay times and to make further critical tests of the theory, as outlined in Section C.

Some final remarks on experiments of others are needed to relate this theory to the known facts. In (Ref. 19) it is stated that aluminized propellants are more difficult to ignite than non-metallized propellant. This would agree with the theory, if the result of adding aluminum is to decrease the volumetric fraction of fuel. (See Equation (6)). In (Ref. 19) attention is called also to the effect of cold ambient temperatures in lengthening the ignition times. This would follow from Equation (6) and from Equation (2).

In similar experiments on ignition of solid propellants, employing the flow of hot gas from the compression chamber of a shock tube through a short tubular section of propellant, Ryan and Baer (Refs. 3 and 4) have found it possible to ignite perchlorate propellants in pure nitrogen, but the ignition times were ten to fifty times longer than those encountered here. One must conclude that, in this case, the more extended heating time finally resulted in decomposition of the hard-to-pyrolyze perchlorate, so that oxygen finally entered the gaseous layer where the fuel vapor had already diffused.

Similar vigorous heating must be provided by standard torch-type igniter squibs for practical rockets, since these are generally underoxidized in composition, and would correspond to shock tube tests with inert gas. If excess oxygen were

provided in the igniter composition, more prompt ignition might be achieved, or a reduction in igniter mass might be possible. The relative promptness of igniters made of rolled sheets of metal-oxidant mixtures in a small amount of binder (Ref. 19) is probably due to the abundance of free oxygen liberated by the crystalline oxidizer, as well as the high temperatures generated by the burning metal powder.

E. Conclusion

Ignition of solid propellants of the ammonium perchlorate type has been accomplished in a shock tube in times of the order of a millisecond, despite the relatively modest temperature, less than 200 C, developed at the surface of the propellant. The explanation of this performance rests on a gas phase theory of ignition, entirely different from the solid phase theory that had been developed by Altman in 1950 and by Hicks in 1954 and which has been accepted by others since that date. The evidence in favor of the new theory lies mainly in the observed strong effect of oxygen in the igniter gas on the ignition delay. A further indication of its validity is that it predicts the correct order of ignition delay (about 1 millisecond) in these experiments, with no adjustable parameters or "fudge" factors and no assumed "global" activation energy. The experimental work is continuing, with improved methods for measuring ignition delay, in order to provide a closer quantitative check of the theory.

REFERENCES

1. Altman, A., Grant, A., "The Thermal Theory of Solid Propellant Ignition by Hot Wires," Fourth Symposium on Combustion, Baltimore, Williams and Wilkins Company, 1950, p. 158.
2. Churchill, S. W., Kruggel, R. W., Brier, J. C., "Ignition of Solid Propellants by Forced Convection," A.I.Ch.E. Journal, December, 1956, p. 568.
3. Baer, A. D., Ryan, N. W., Salt, D. L., "Fundamental Studies of Ignition by Means of a Shock Tube," ARS Preprint No. 1059, presented at the American Rocket Society Meeting on Solid Propellant Rocket Research, Princeton, N. J., January 28, 1960.
4. Baer, A. D., "Composite Propellant Ignition," Ph.D. thesis, University of Utah, March, 1959.
5. Hicks, B. L., "Theory of Ignition Considered as a Thermal Reaction," J. Chem. Phys., Vol. 22, No. 3, March, 1954, p. 414.
6. Cook, M. A., Olson, F. A., "Chemical Factors in Propellant Ignition," A.I.Ch.E. Journal, 1, 391, 1955.
7. Rice, O. K., Ginell, R., "The Theory of the Burning of Double-Base Rocket Powders," Journal of Physical and Colloid Chemistry, Vol. 54, No. 6, June, 1950, p. 885.
8. Parr, R. G., Crawford, B. L., "A Physical Theory of Burning of Double Base Rocket Propellants," Journal of Physical and Colloid Chemistry, Vol. 54, No. 6, June, 1950, p. 929.
9. Summerfield, M., Sutherland, G. S., Webb, M. J., Taback, H. J., and Hall, K. P., "Burning of Ammonium Perchlorate Propellants," ARS Preprint No. 737-58, presented at the American Rocket Society's 13th Annual Meeting, New York, November, 1958.
10. Fishman, unpublished work, Stanford Research Institute, 1959.
11. Summerfield, M., McAlevy, R. F., "The Shock Tube as a Tool for Solid Propellant Ignition Research," Jet Propulsion, Vol. 28, No. 7, July, 1958, p. 478. AD-112-76
12. Langwell, J. P., Weiss, M. A., "High Temperature Reaction Rates in Hydrocarbon Combustion," Industrial and Engineering Chemistry, Vol. 4, No. 8, August, 1955, p. 1635.
13. Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill Book Company, New York, 1958, p. 274.
14. Chaiken, R. F., Anderson, W. H., "The Role of Binder in Composite Propellant Combustion," Paper presented by the 135th Meeting of the American Chemical Society, Symposium on Plastics and Elastomers in Rockets, Atlantic City, New Jersey, September 13-18, 1959.

15. Chaiken, R. F., Personal Communication, January 1960.
16. Shultz, R., Green, L., and Penner, S.S., "Studies of the Decomposition Mechanism, Erosive Burning, Sonance and Resonance for Solid Composite Propellants," Selected Combustion Problems, Vol. III, Butterworth Scientific Publications, London 1959.
17. Carslaw, H. S., "Conduction of Heat in Solids," Oxford (Clarendon) Press, 1959, p.88.
18. Crank, J., "The Mathematics of Diffusion," Oxford (Clarendon) Press, 1956, p.31.
19. Rabern, J. W., "Systems for Ignition of Solid Propellants," ARS Preprint No.977-59, presented at ARS 14th Annual Meeting, Washington, D.C., November 1959.

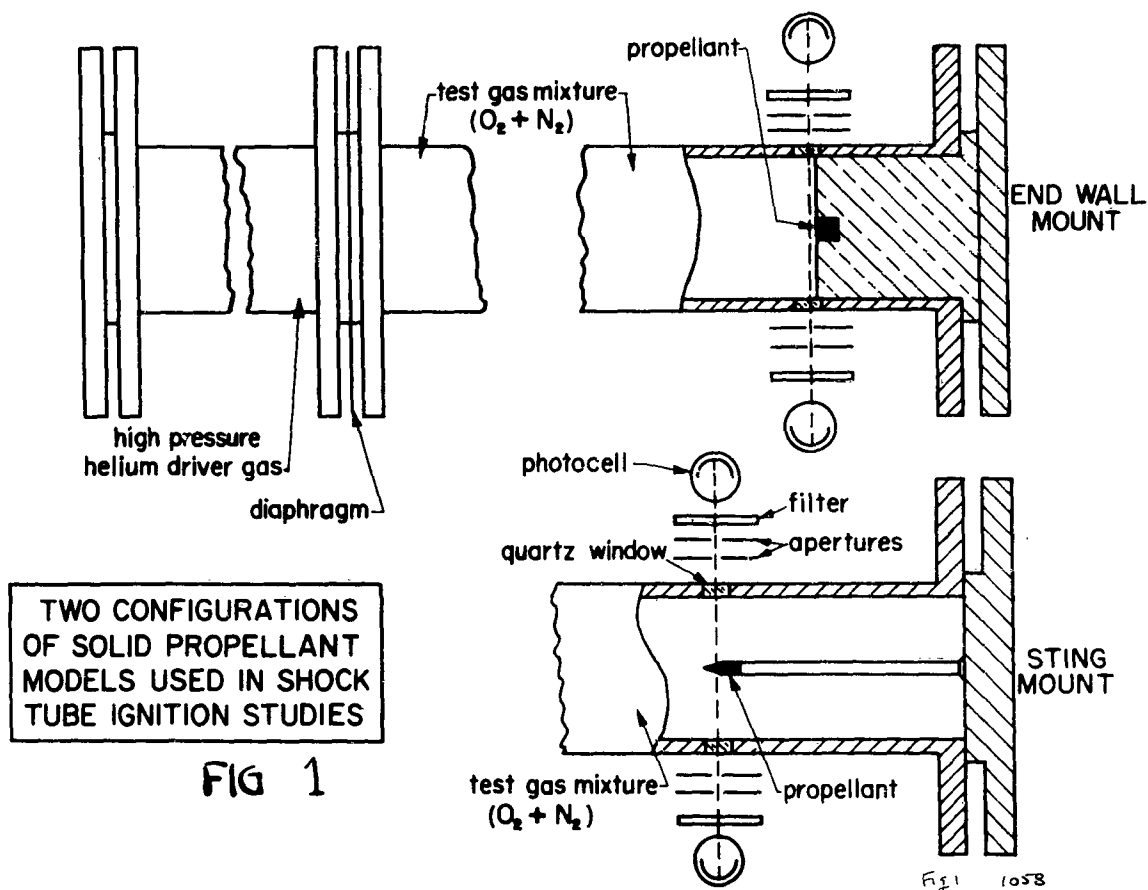
FIGURE LEGENDS

FIGURE	TITLE
1.	Two configurations of solid propellant models used in shock tube ignition studies.
2.	Theoretical increment of end wall surface temperature produced by shock wave reflection. (Correction: Replace 10^{-3} with 10^{-2})
3.	Photographic sequences showing ignition of propellant samples in shock tube.
4.	Photographic sequences showing ignition of sting mounted propellant samples. Faulty model shows premature ignition at microscopic crack between propellant and inert aluminum tip. Later models were protected at all joints by water-glass-asbestos film.
5.	Typical photocell output traces. The initial pulse on each trace is the light emission of the reflected shock. Traces (a) and (b) were made without propellant, traces (c) and (d) with propellant.
6.	Temperature and vaporized fuel distributions at $\frac{1}{10}$ and 1 millisecond after shock wave reflection.
7.	Qualitative representation of fuel vapor "overtaking" hot gas "front".
8.	Linear pyrolysis rates of two fuels and ammonium perchlorate. Solid lines represent experimental data. Dashed lines are extrapolations for purpose of this paper.

FIGURE

TITLE

9. Determination of location of ignition in gas phase. See Equations (6) and (7) for use of this graph to compute X^* . (Correction: Insert E in denominator of F function)
10. Measured ignition delays for two propellants, end wall mounted samples in shock tube. (Preliminary data.)
11. Combustion of ammonium perchlorate in a stream of propane flowing upward through a flat porous disk. The stream of propane is burning with the external air in an outer conical diffusion flame, while the burning perchlorate crystals are in the middle of the disk.



TWO CONFIGURATIONS OF SOLID PROPELLANT MODELS USED IN SHOCK TUBE IGNITION STUDIES

FIG 1

THEORETICAL INCREMENT OF END WALL SURFACE TEMPERATURE PRODUCED BY SHOCK WAVE REFLECTION

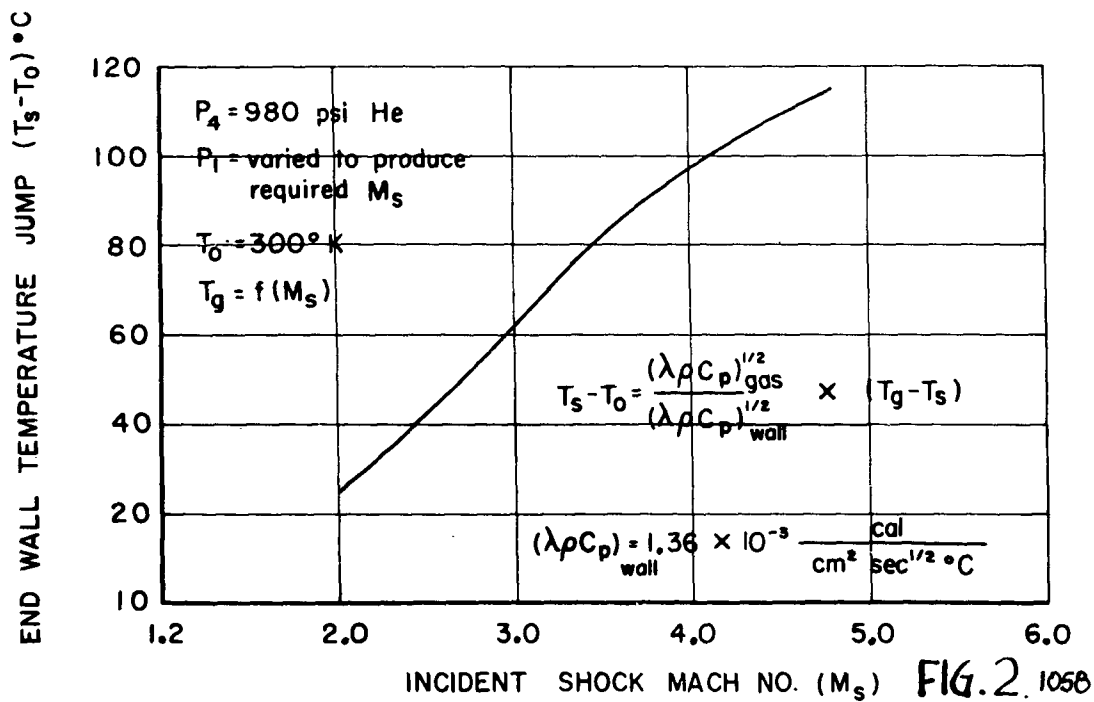
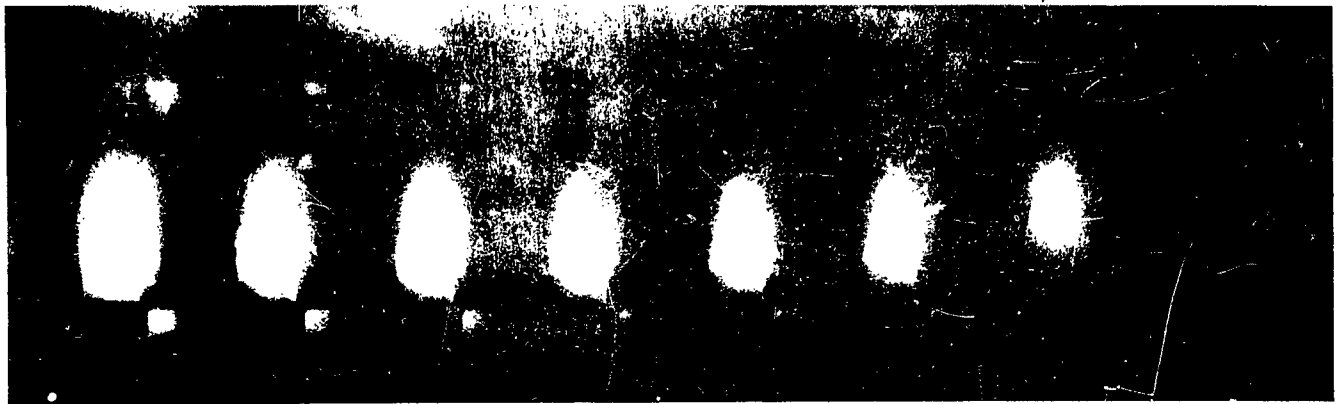


Fig. 2 1058

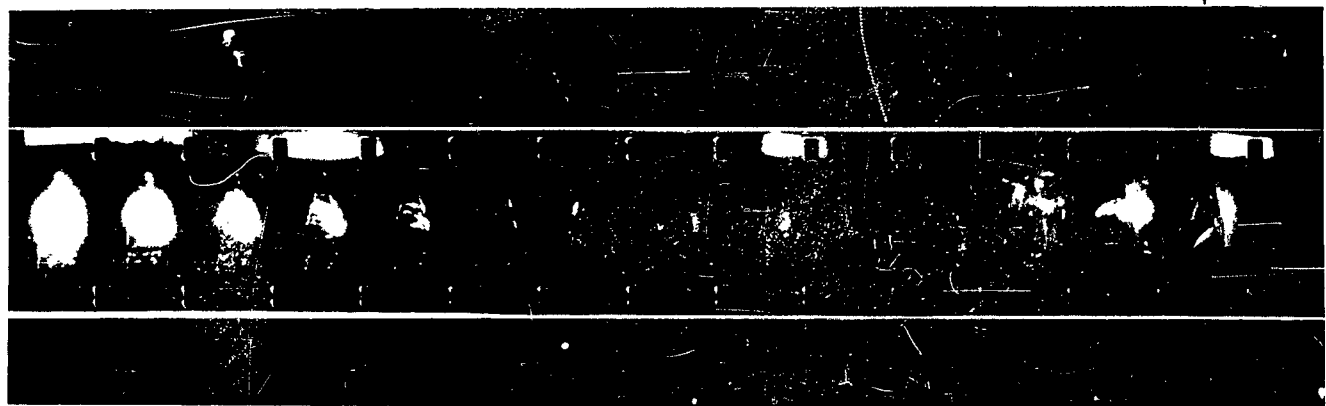
Passage of Reflected Shock →



Polystyrene + A.P. Propellant, 53% O_2 , 1000 Frames/Sec

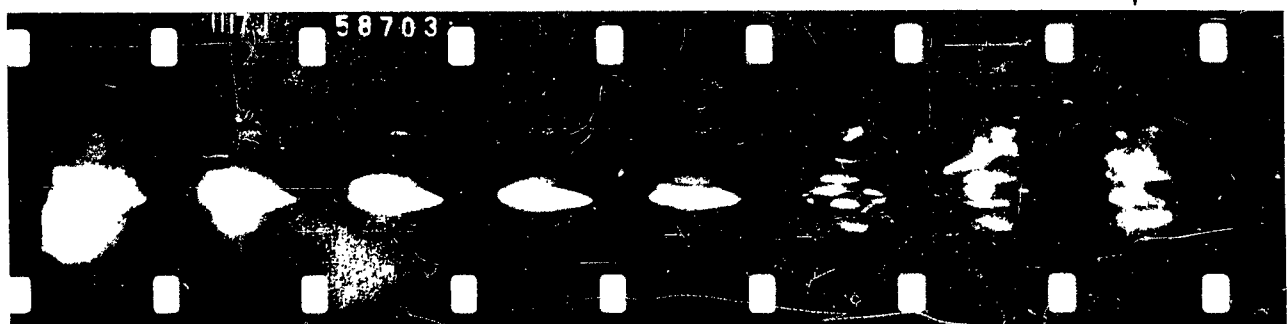
← Time

Passage of Reflected Shock →



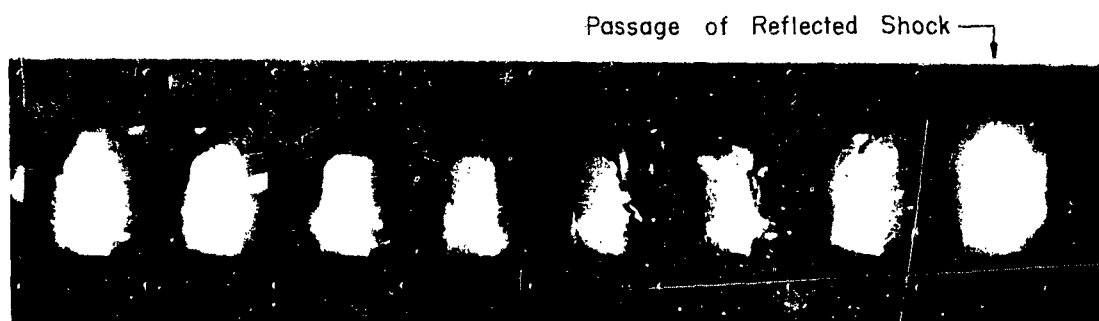
Epoxy Resin + A.P. + Ferric Oxide Propellant, 46% O_2 , 5000 Frames/Sec

Passage of Reflected Shock →

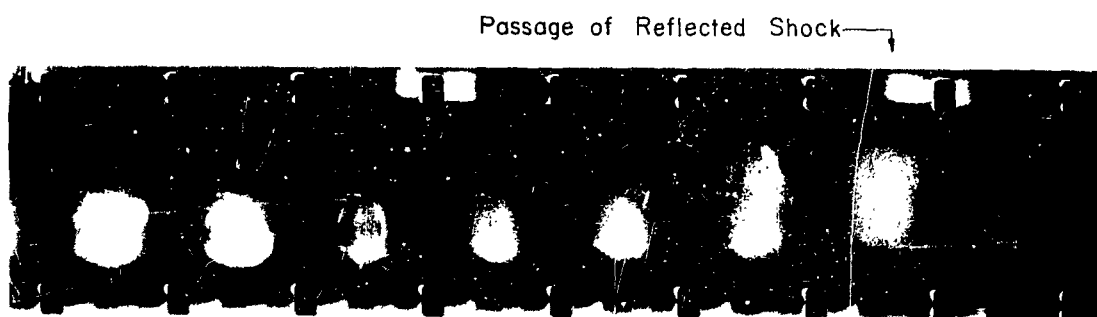


Epoxy Resin + A.P. + Ferric Oxide Propellant, 75% O_2 , 3000 Frames/Sec

FIG. 3 IGNITION OF PROPELLANT SAMPLES IN SHOCK TUBE (1058)

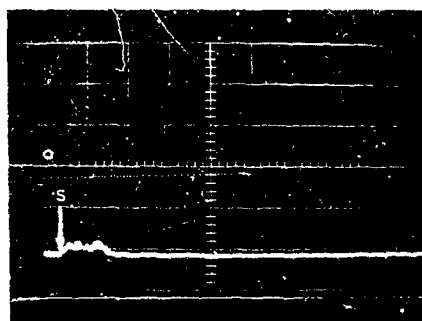


(a) Round Nose Propellant Sample, 75 % O_2 , 3000 Frames/Sec

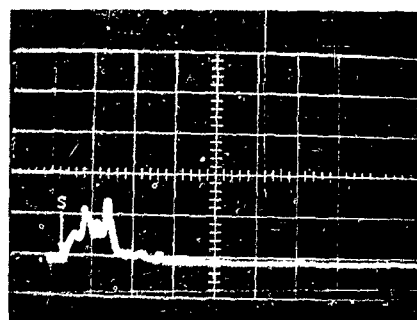


(b) Faulty Model, 46 % O_2 , 4000 Frames/Sec

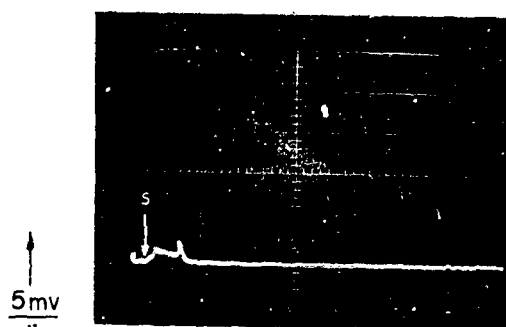
FIG 4 IGNITION OF STING MOUNTED PROPELLANT SAMPLES



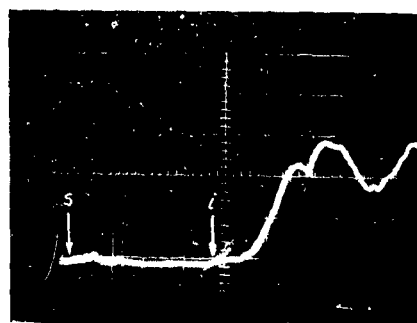
(A) Clean Tube



(B) Contaminated Tube



(C) No Ignition



(D) Ignition

5mv
div

500 μ sec
div

FIG. 5 TYPICAL PHOTOCELL OUTPUT TRACES (1058)

TEMPERATURE AND VAPORIZED FUEL DISTRIBUTIONS
AT 10 AND 1 MILLISECOND AFTER SHOCK WAVE REFLECTION

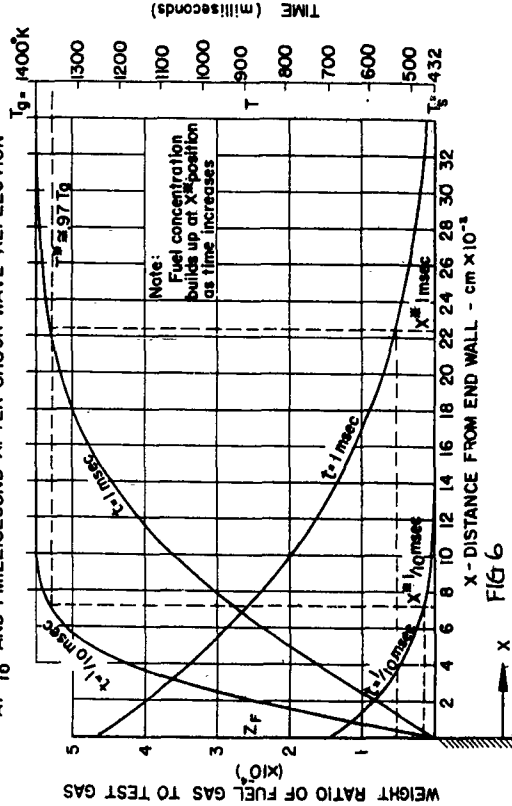


FIG 6

QUALITATIVE REPRESENTATION OF FUEL
VAPOR "OVERTAKING" HOT GAS "FRONT"

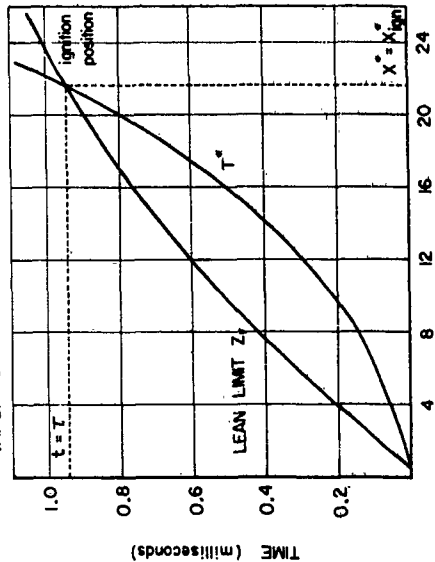


FIG 7 DISTANCE FROM END WALL (10^{-3} cm)

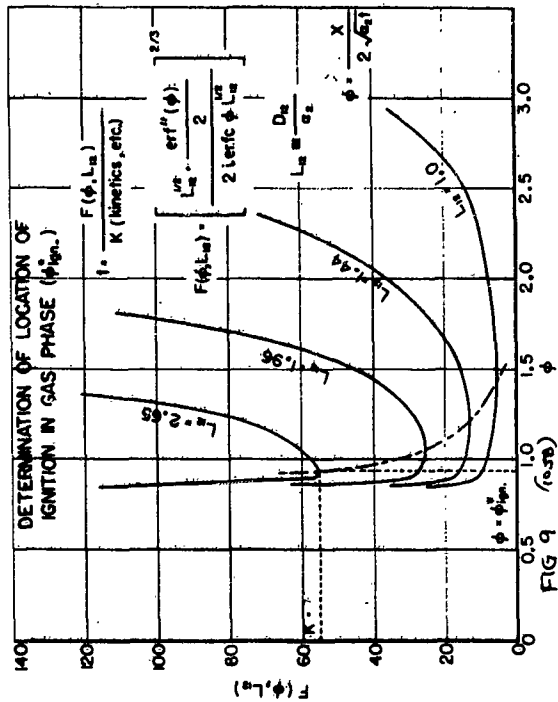
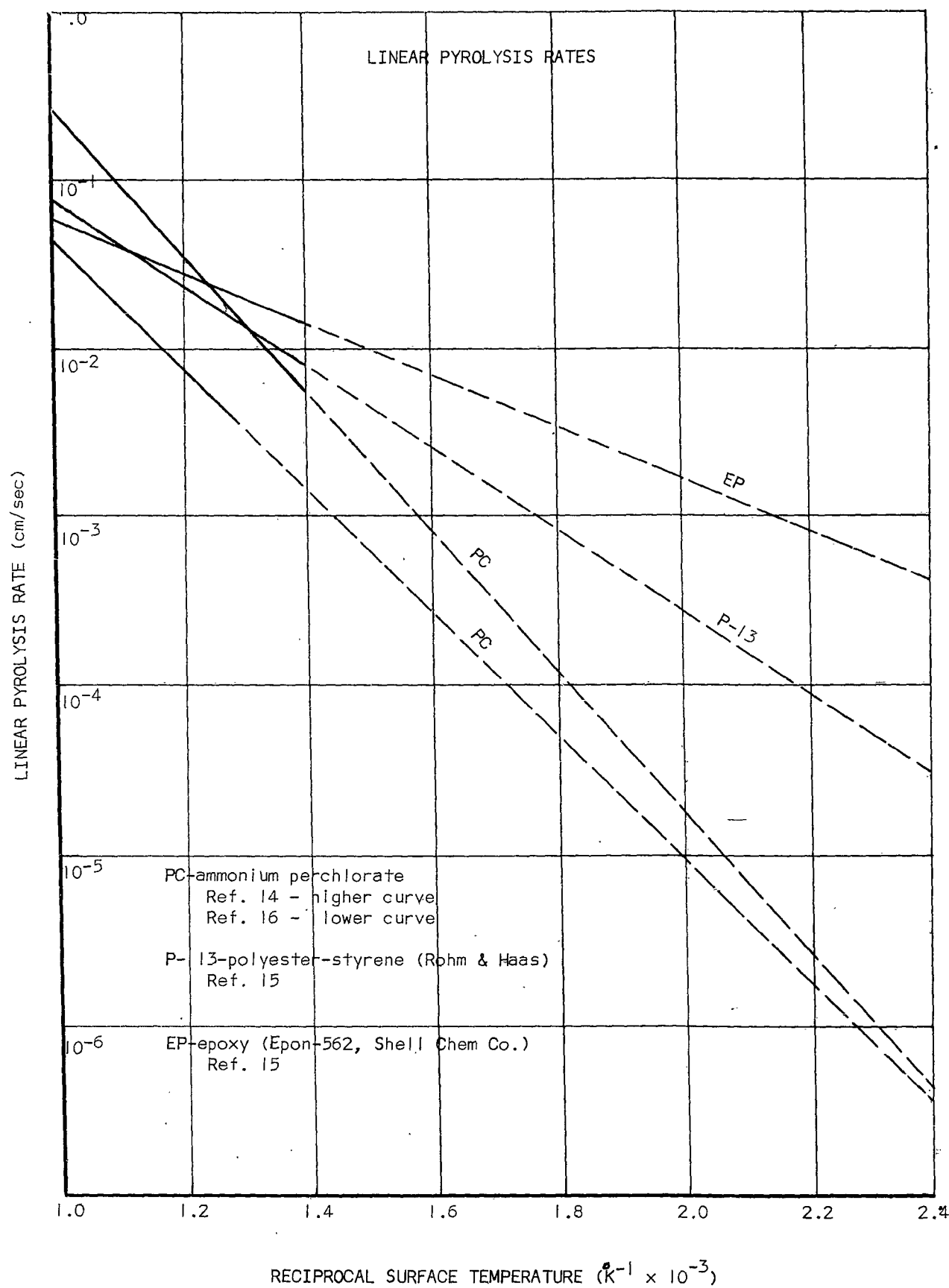
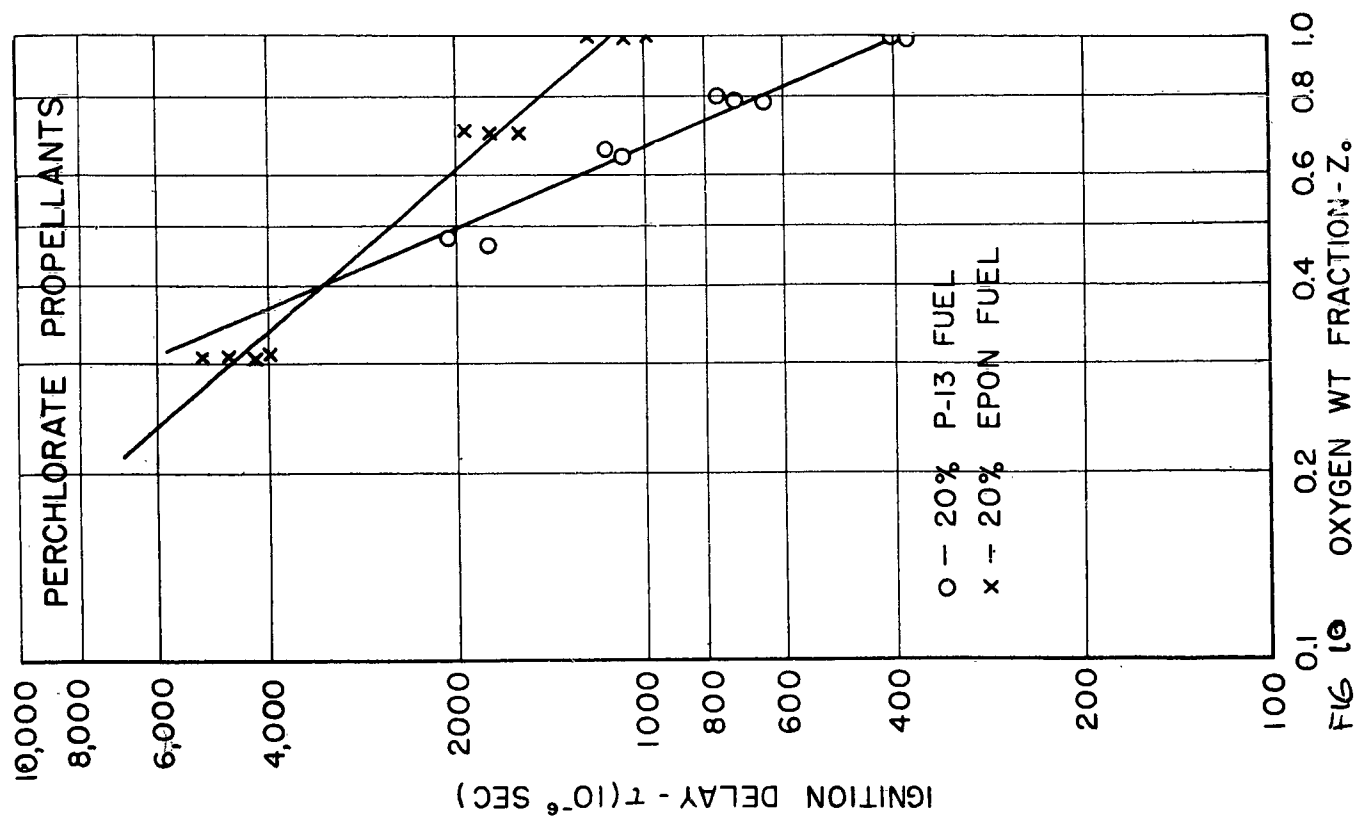


FIG 9





COMBUSTION OF AMMONIUM PERCHLORATE
IN STREAM OF PROPANE
FIG 11 1058

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